Characterization of Advanced Solid Rocket Nozzle Materials

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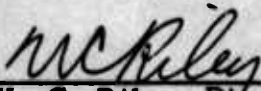El Segundo, Calif. 90245

18 December 1975

Interim Report

Prepared for

AIR FORCE ROCKET PROPULSION LABORATORY
Edwards Air Force Base, Calif. 93523

SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
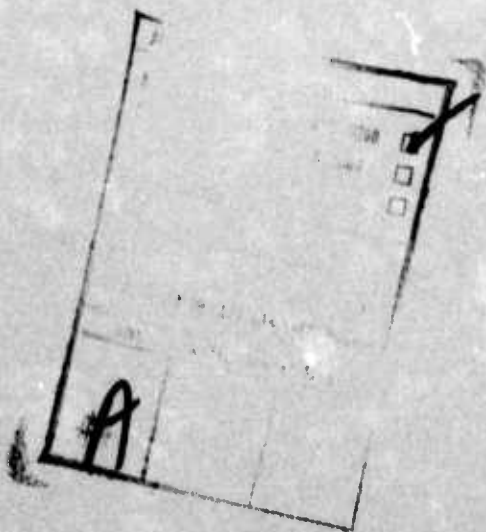P.O. Box 92960, Worldway Postal Center
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This technical report has been reviewed and is approved for publication.
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FOR THE COMMANDER

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SAMSO-TR-75-301	**2. GOVT ACCESSION NO.**	**3. RECIPIENT'S CATALOG NUMBER**
4. TITLE *(and Subtitle)* CHARACTERIZATION OF ADVANCED SOLID ROCKET NOZZLE MATERIALS.		**5. TYPE OF REPORT & PERIOD COVERED** Interim rept.,
		6. PERFORMING ORG. REPORT NUMBER TR-0076(6622)-1
7. AUTHOR(s) Jay G. Baetz		**8. CONTRACT OR GRANT NUMBER(s)** F04701-75-C-0076
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, Calif. 90245		**10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS** 29 p.
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Rocket Propulsion Laboratory Edwards Air Force Base, Calif. 93523		**12. REPORT DATE** 18 December 1975
		13. NUMBER OF PAGES 26
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)* Space and Missile Systems Organization Air Force Systems Command Los Angeles, Calif. 90009		**15. SECURITY CLASS. *(of this report)*** Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Carbon-Carbon	Characterization
Pyrolytic Graphite	Microstructures
Solid Rocket Nozzle	Tailorability

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*
A program is presented for the characterization of advanced carbon-carbon and pyrolytic graphite materials for solid rocket nozzle application. The various elements of the program are examined, and techniques for measuring individual elements are discussed. Particular attention is directed toward several unique techniques that have been developed especially for this program. Data are presented that show the relationship of material properties and microstructural characteristics to fabrication processing conditions.

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19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

The use of key properties characterization to fingerprint carbon-carbon and pyrolytic graphite materials within their generic families is postulated.

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FIGURES

I. INTRODUCTION

The next generation of solid rocket nozzles will most likely use materials that respond to the rocket motor exhaust environment in a complex series of interrelated thermomechanical and thermochemical reactions. Success or failure of these materials will depend on the ability to understand these responses in terms of individual material characteristics. In addition, these characteristics must be quantified in terms of favorable and unfavorable responses and the materials tailored to yield the greatest safety margin.

Two of the more promising advanced solid rocket nozzle material families are pyrolytic graphites and carbon-carbons. In order to provide direction for the development of these materials, a program to characterize them has been implemented. This program contains three basic elements:

1. Characterization by defining material microstructure. This element includes qualitative techniques, such as metallograph and scanning electron microscope (SEM) photomicroscopy, and quantification of the microstructural characteristics through unit cell dimensioning and optical discernment of the anisotropy state.

2. Characterization by measuring key mechanical and thermal properties.

3. Characterization by monitoring certain special material properties. This element includes examination of chemadsorption characteristics and porosity distributions of both carbon-carbons and pyrolytic graphites. These properties play key roles in the material response to the thermochemical environment of the rocket motor. Determination of the residual stress is also a vital part of this element.

Since both pyrolytic graphites and carbon-carbons undergo processing at elevated temperatures, some severe stress fields are locked into the closed nozzle structure during the cool-down process. These stresses can have a profound effect on performance.

Highlights of the characterization study are presented herein. The objectives of this paper are to acquaint the reader with the mechanics of the characterization techniques used and to relate the understanding of the resulting material properties to performance in a solid rocket motor environment.

II. CHARACTERIZATION OF CARBON-CARBON MATERIALS

A number of two and three dimensionally reinforced carbon-carbon materials are of interest as candidates for solid rocket nozzle components. Characterization of the two dimensionally reinforced (2D) materials is well under way. Work on the three dimensionally reinforced (3D) carbon-carbons is awaiting delivery of samples. The data presented are therefore limited in scope, but because the major emphasis here is on examination of the mechanics of characterization, the efforts involving 2D carbon-carbons will suffice to illustrate the techniques used. The characterization study was carried out by qualitative microstructure examination with both the metallograph and the SEM. Thermal expansion excursions were used to represent the conventional properties measurements. Porosity distributions were conducted as special properties measurements. The results of the study are discussed below.

A. MICROSTRUCTURE

The metallograph and SEM are excellent tools for use in examining the structure of carbon-carbons. Detailed visual evidence can be obtained of both the as-fabricated and the post-tested parts. The metallograph is most suited to examination of polished sections that are normal to the fired or proposed fired surface. The SEM, on the other hand, is most suited to examination of the fired surfaces themselves. Photomicrographs (Figs. 1 and 2) of two potential nozzle candidates designated Pyrocarb 903 and Pyrocarb 409M reveal distinct differences characteristic of their processing and basic starting materials. Pyrocarb 903 is a flat laminate material that consists of a carbonized polyacrylocnitrile (PAN) fabric in a phenolic resin matrix that is subsequently pyrolyzed and carbonized. Pyrocarb 409M is comprised of a carbonized rayon base reinforcement in a carbon vapor deposit (CVD) matrix. Both are produced by Hitco. Comparison of the surface condition of each material after firing (Figs. 3 and 4) indicates the distinct difference in their response to the rocket motor environment.
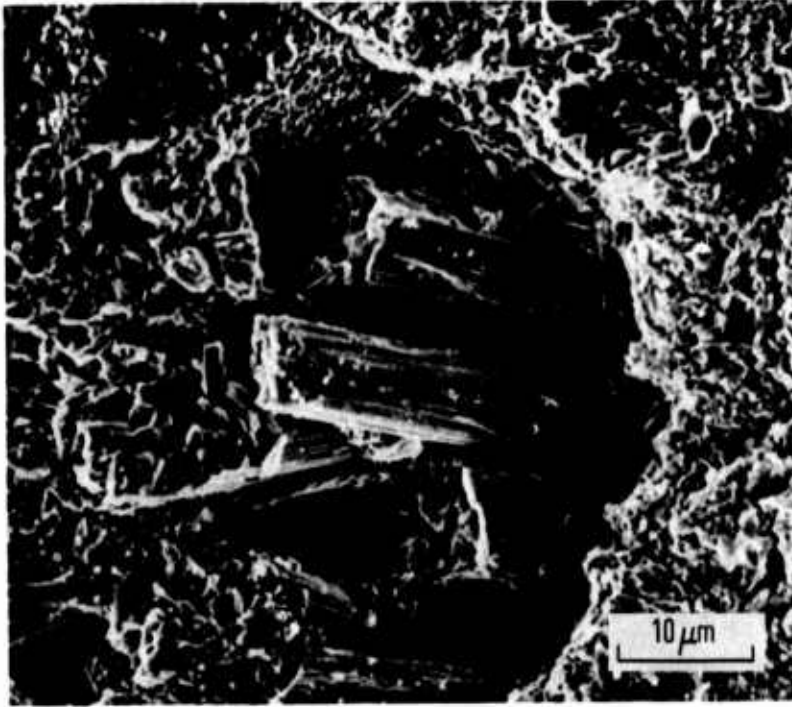
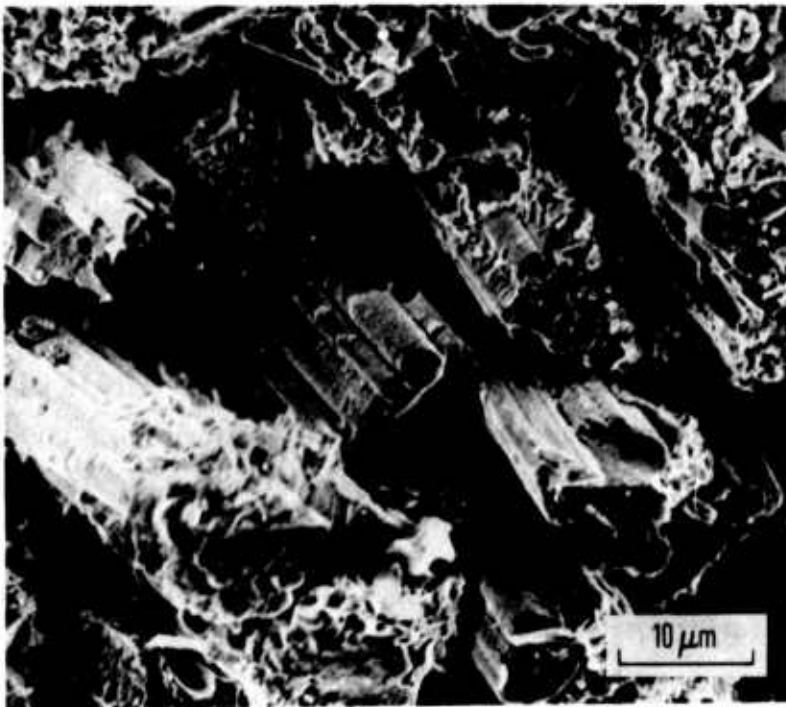Figure 1.   Pyrocarb 903 Backface

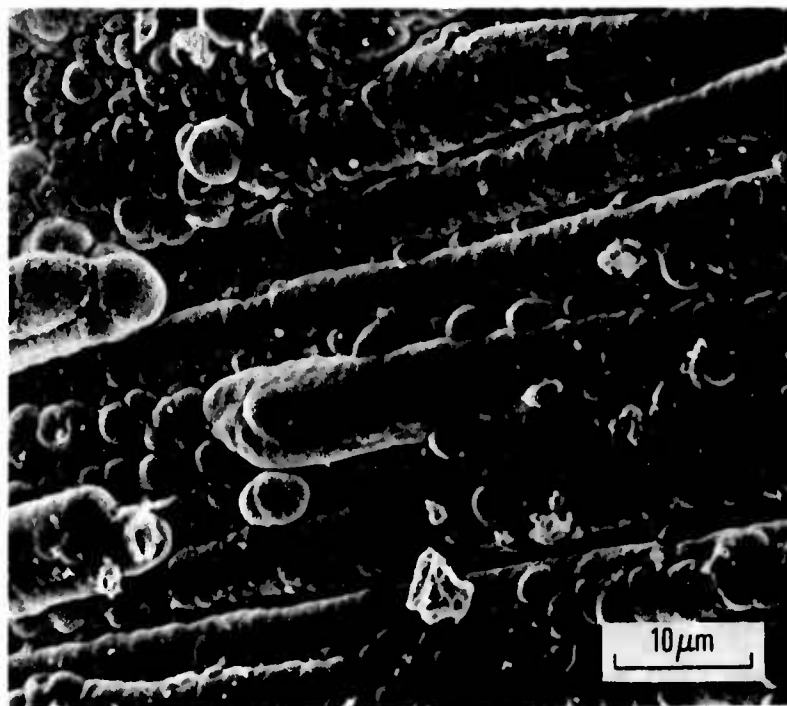Figure 2.   Pyrocarb 409M Backface
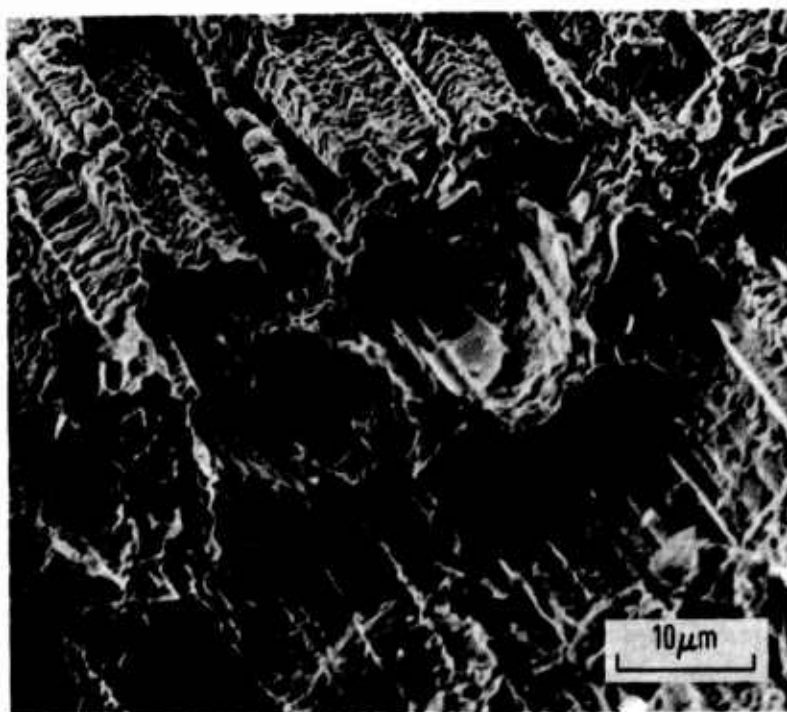
Figure 3.   Pyrocarb 903 Fired

Figure 4.   Pyrocarb 409M Fired

The photomicrographs illustrate that the regression of the Pyrocarb 903 is primarily due to preferential thermochemical attack of the matrix material with subsequent mechanical removal of the reinforcement. The mass removal mechanism for the 490M, on the other hand, appears to be driven predominantly by mechanical removal of individual fibers below the fiber-matrix interface, as is clearly shown by the sharp cleavage planes of the recessed fibers in Fig. 4. In other words, the matrix of the 409M is more resistant to the erosion-corrosion process than the reinforcement.

From these observations, it might be concluded that a valid endeavor would be to study the possibility of combining PAN reinforcement in a CVD matrix for increased erosion resistance. Obviously, this is but one of several data inputs that are required before such a conclusion can be considered valid, and these represent but two of a myriad of candidate carbon-carbons systems. They do, however, illustrate the way in which microstructural properties are vital toward gaining an understanding of the response of a given material to the rocket exhaust environment. From this comes one of the data points needed to give direction to the ultimate upgrading of the material's performance.

B.   THERMAL EXPANSION

Thermal expansion excursions to the rocket motor firing temperatures were selected as the thermal or mechanical property most sensitive to variations in both the processing conditions and the rocket motor environment. Specifically, the thermal expansion characterizations of Pyrocarb 903 were selected to demonstrate two primary points that illustrate the need for precise definition of this key material property. The thermal expansion excursions of several versions of Pyrocarb 903 measured in the with-ply direction are shown in Fig. 5. The only difference among these materials was density, yet the range of thermal expansions is relatively severe. The reverse relationship exists between density and thermal expansion for 903 in the cross-lamina direction. The effect of the thermal exposure of the rocket motor on thermal expansion is illustrated in Fig. 6. In this case, the same material exhibited two distinct thermal properties that were dependent only on exposure
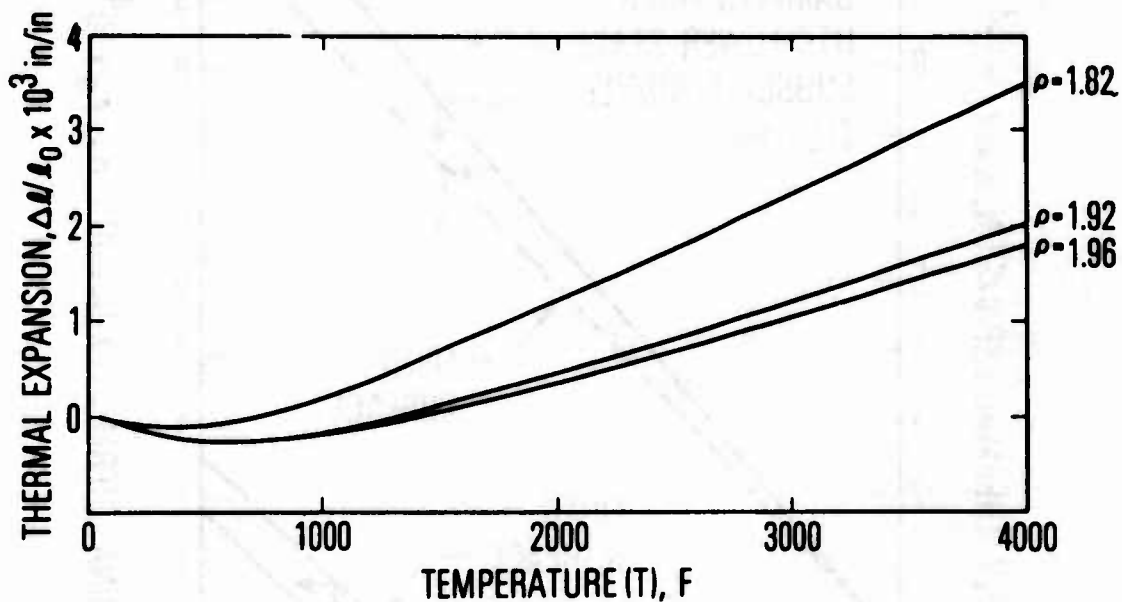
Figure 5. With-Lamina Thermal Expansion of Pyrocarb 903
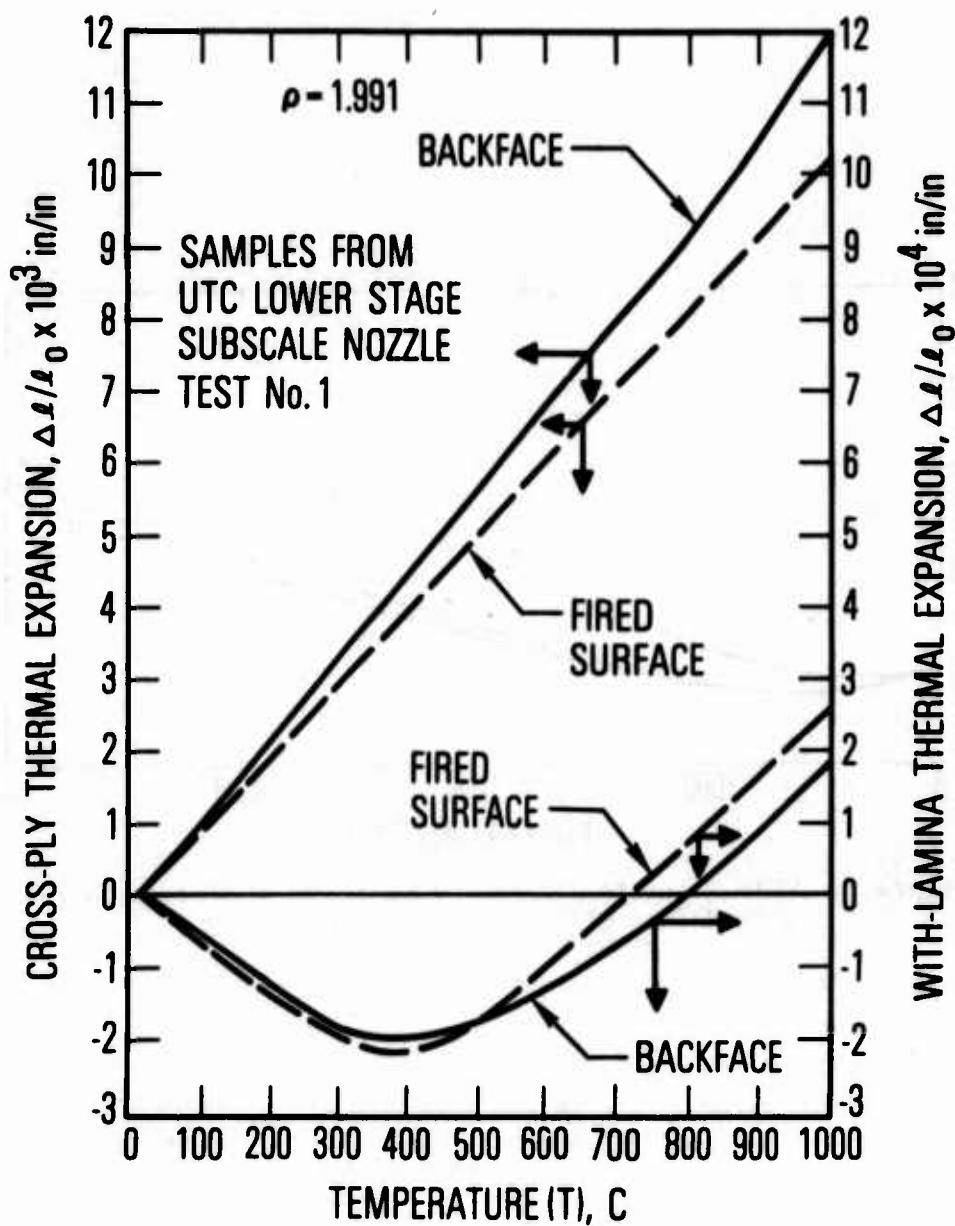with Effect of Density Variations Shown

Figure 6. Thermal Expansion of Pyrocarb 903

to the rocket firing. The materials were taken from the same billet. Replicate measurements were made. The key point to be made here is that it is not sufficient to measure thermal expansion of a material, record the data, and continue to draw on this literature value for input to a thermal analysis. Less obvious is the implication that it may also be invalid to measure thermal expansion under quasi-static laboratory conditions and apply these data to a meaningful analysis. Gerald Driggers of Southern Research Institute has postulated the need for a dynamic approach to all materials properties measurements. [1] These data tend to support his arguments.

C.   POROSITY DISTRIBUTION

It has been proposed that, within all carbon systems, density is the key element in determining erosion rate. [2] Others have maintained that pore size and pore-size distribution are the true keys to performance, particularly in a reentry environment. [3] In any case, because the two properties are so closely related, it behooves us to examine porosity as a key property. This has been done with the goal of defining exactly what traits within porosity are the true drivers from the standpoint of performance. Within the scope of the materials examined, density and porosity varied in parallel; thus, no direct delineation on material performance can be made. On the other hand, some key traits of the property porosity were uncovered that may subsequently provide a clue to material performance. The pore-size distribution characteristics of Pyrocarbs 903 and 409M are discussed here because they have marked differences in microstructural response to the rocket motor environment. The pore-size distributions of Pyrocarb 903 before and after firing are graphically illustrated in Figs. 7 and 8, respectively. Similar distribution plots for Pyrocarb 409M are sh... in Figs. 9 and 10. The marked differences noted in the microstructural response of each material to firing environment are shown in their pore-size distribution response. Comparison of Figs. 7 and 8 indicates that Pyrocarb 903 initially contains some relatively large-size pores as well as a group of moderate-size pores, but that after firing, the number of large pores is drastically reduced. Pyrocarb 409M,

Figure 7

SAMPLE WEIGHT, g 0.1663
APPARENT DENSITY, g/cc 1.9205
REAL DENSITY, g/cc 2.1000
cc VOIDS/g, cc/g 0.0445
PERCENT VOID VOLUME 8.5459

PORE VOLUME, %

CUMULATIVE PORE VOLUME, %

139.8 99.0 43.6 29.9 20.9 17.0 9.6 6.0 4.67 3.43 2.95 2.07 1.72 1.35 0.98 0.61 0.345 0.198 0.142 0.069 0.035 0.023 0.018 0.015 0.013

PORE DIAMETER, μm

Figure 7.   Pore-Size Distribution of Pyrocarb 903
Before Firing

Figure 8

SAMPLE WEIGHT, g 0.2378
APPARENT DENSITY, g/cc 1.9492
REAL DENSITY, g/cc 2.1251
cc VOIDS/g, cc/g 0.0425
PERCENT VOID VOLUME 8.2788

PORE VOLUME, %

CUMULATIVE PORE VOLUME, %

138.7 98.7 43.5 29.9 20.9 17.0 9.6 6.0 4.67 3.43 2.95 2.07 1.72 1.35 0.98 0.61 0.344 0.198 0.142 0.069 0.035 0.023 0.018 0.015 0.013
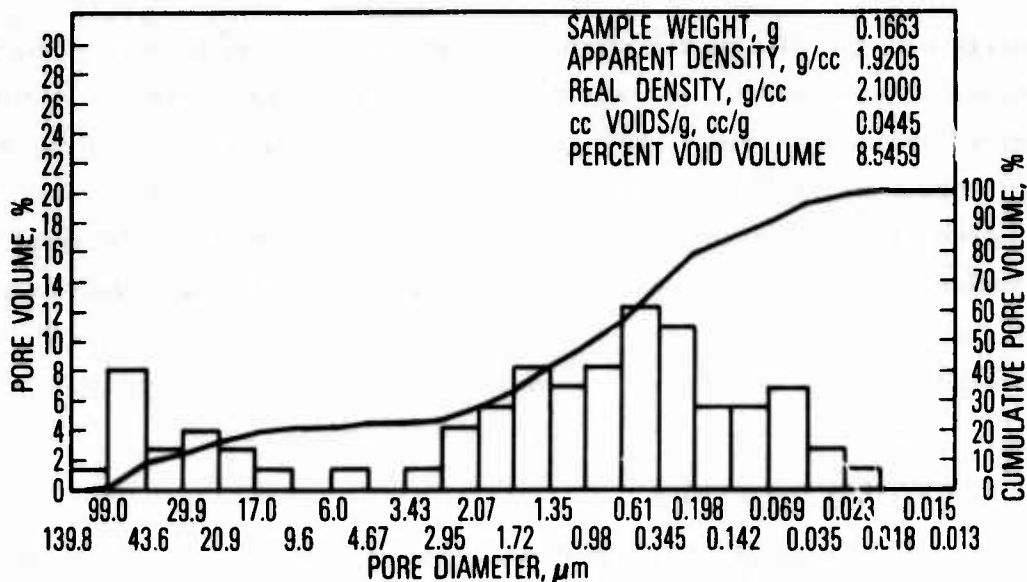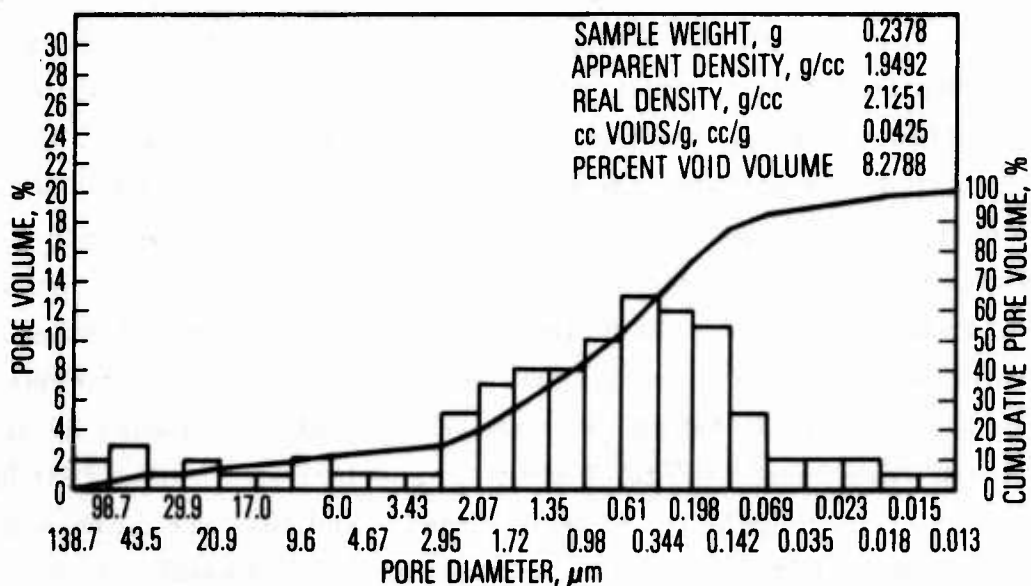
PORE DIAMETER, μm

Figure 8.   Pore-Size Distribution of Pyrocarb 903
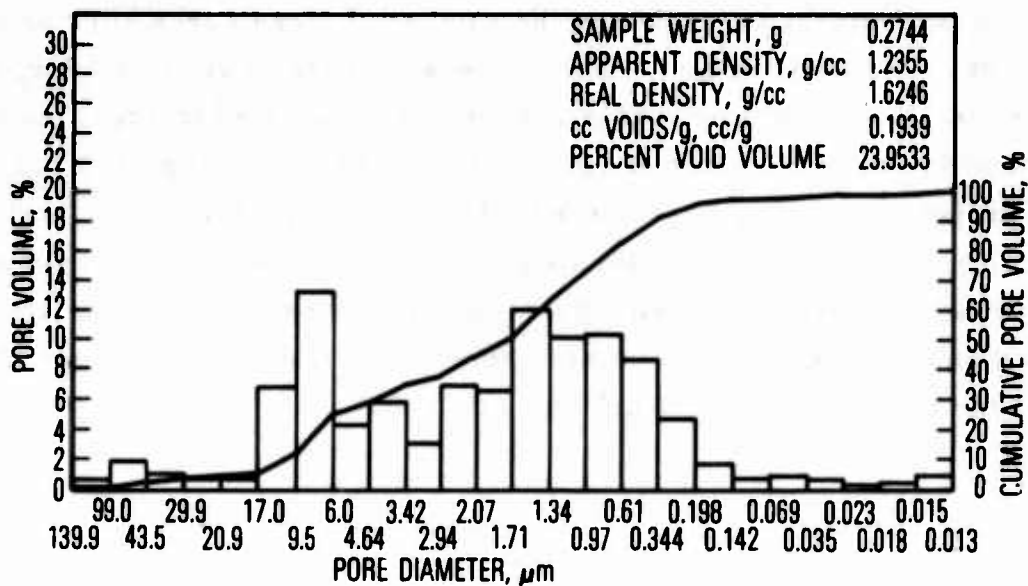After Firing

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Figure 9. Pore-Size Distribution of Pyrocarb 409M
Before Firing
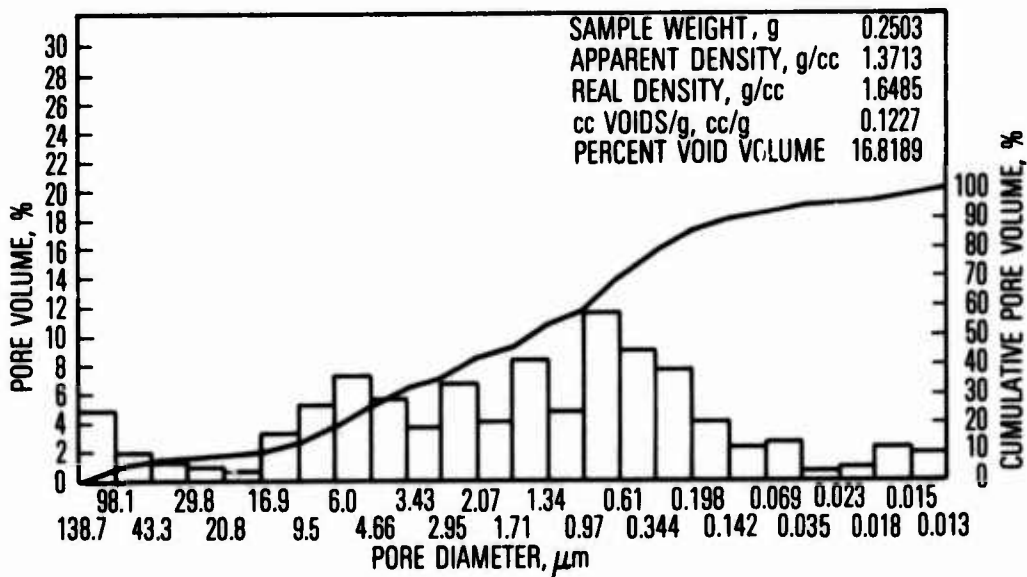
Figure 10. Pore-Size Distribution of Pyrocarb 409M
After Firing

however, shows a marked increase in the number of large pores after exposure to the rocket motor environment. This increase occurs in spite of a large reduction in overall void volume. This response is illustrated in Figs. 9 and 10. The task now becomes a matter of equating these observed responses in the material property porosity, together with the other characterized properties, to material performance. The ultimate goal is to understand what elements go into making a superior performing material in the rocket motor environment and then direct our efforts toward achieving that material. These efforts represent the initial step toward achieving this goal.

III. CHARACTERIZATION OF PYROLYTIC GRAPHITE MATERIALS

Although the primary objective to characterize the various properties of pyrolytic graphite materials is the same as for the carbon-carbons, significant differences in the two structures dictate that flexibility must be maintained in determining the key properties that should be examined in the characterization of each. Some characteristics of pyrolytic graphites that were evaluated were not considered significant or applicable to the carbon-carbon materials. Other properties, such as microstructural comparisons and thermal expansion measurements, are valid for both. The characteristic properties of the pyrolytic graphites that are discussed include both qualitative and quantitative definition of microstructure. Thermal expansion was determined to be representative of the conventional properties measurements. The critical property, residual stress state, was evaluated under the element of special properties measurements. Each of these elements is discussed below.

A. MICROSTRUCTURE

A precise definition of the various qualitative microstructural characteristics of pyrolytic graphites and the role each plays in influencing other conventional material properties and, ultimately, performance itself have long been topics of debate. However, the fact that such a relationship does exist has been demonstrated by Donadio and Pappis[4] and others.[5,6] In attempting to pinpoint the microstructural properties of pyrolytic graphites, we have considered both qualitative and quantitative methods. Some of the basic pyrolytic graphite structures that have been deposited are shown in Fig. 11. Although many others exist, both within these bounds and beyond the extremes, the structures shown represent those whose characteristic properties were examined in this study. Each material has associated with it a distinct set of thermal and mechanical properties and, therefore, a distinct rocket motor response characteristic.
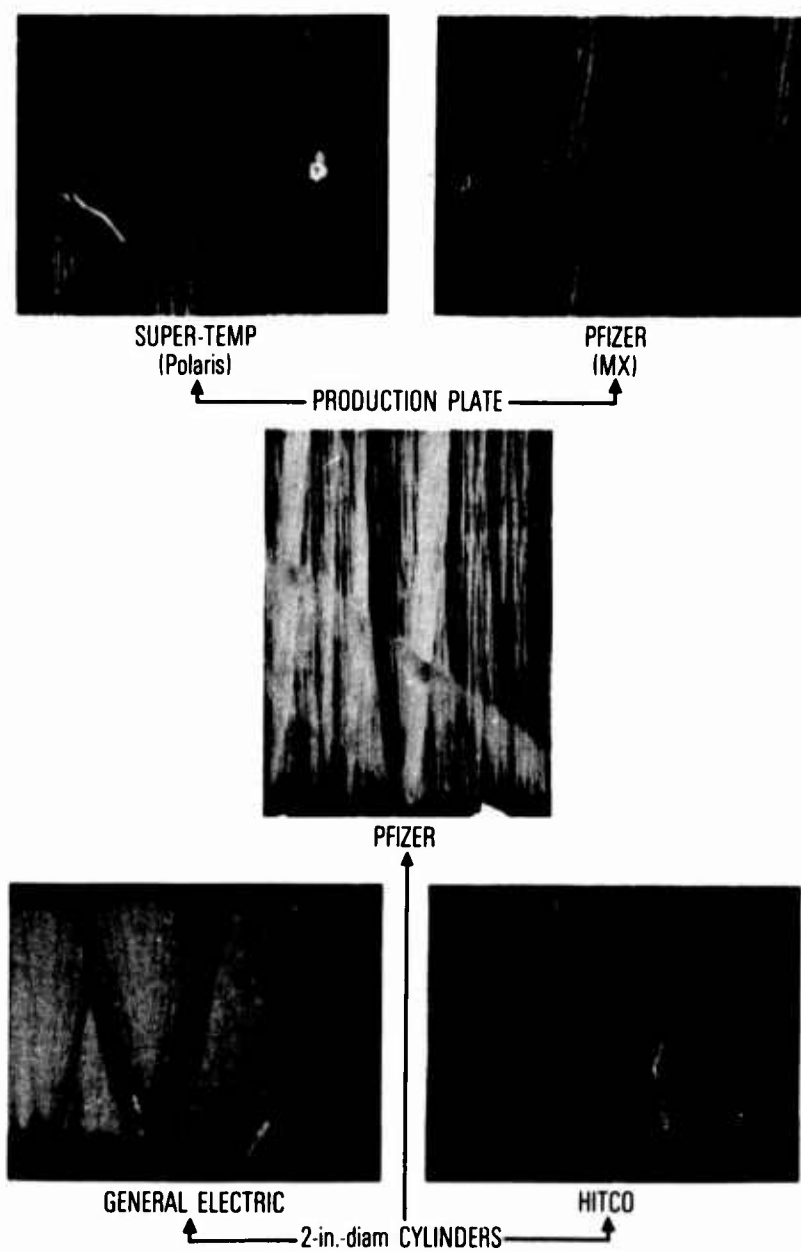
Figure 11. Comparison of Pyrolytic Graphite Microstructures

A sensitive measure of the anisotropic natures of different pyrolytic graphites based on the optical properties of these materials has been adapted from a technique developed by Bomar, Gray, and Eatherly[7] at Oak Ridge National Laboratory. The instrumentation for this technique, as developed at Aerospace, consists of an incident light polarizing microscope instrumented with a variable speed rotating stage drive and a photoresistive sensor mounted on the monocular tube of the microscope. Light striking the sensor is cross-polarized, i.e., plane polarized light is incident on the specimen with the reflected light from the specimen passing through a polarizing "analyzer" that is set at 90 deg to the initial polarizer. In operation, the specimen is leveled and placed on the stage, the stage is rotated at a slow uniform rate, and the resistance of the sensor recorded as a function of stage rotation. The optical signature of three distinct depositions of pyrolitic graphite is shown in Fig. 12. The abscissa ϕ is the angle of stage rotation, and the ordinate is in arbitrary units of intensity decrease. The highest peaks are obtained for material in a highly graphitized state (unit cell height $C_0 = 6.709$ Å). The low peaks are for a conventionally deposited, substrate-nucleated material with a C_0 of 6.854 Å. The major point to be made here is that, although extremes are presented to illustrate the changing signature with changes in cell structure, different optical anisotropy signatures exist for subtle differences in structure, even when no changes in x-ray definition of cell structure such as C_0 exist. It is anticipated that this sensitive technique will permit an accurate prediction to be made of shifts in thermal and mechanical properties that occur with subtle changes in the basic pyrolytic graphite structure.

B.   THERMAL EXPANSION

The property of thermal expansion plays a key role in the characterization of anisotropic materials such as pyrolytic graphites. Relatively minor alternations in structure induced through small deposition variations can result in some severe changes in thermal expansion. These changes, in turn, result in materials with distinctly different response characteristics to the
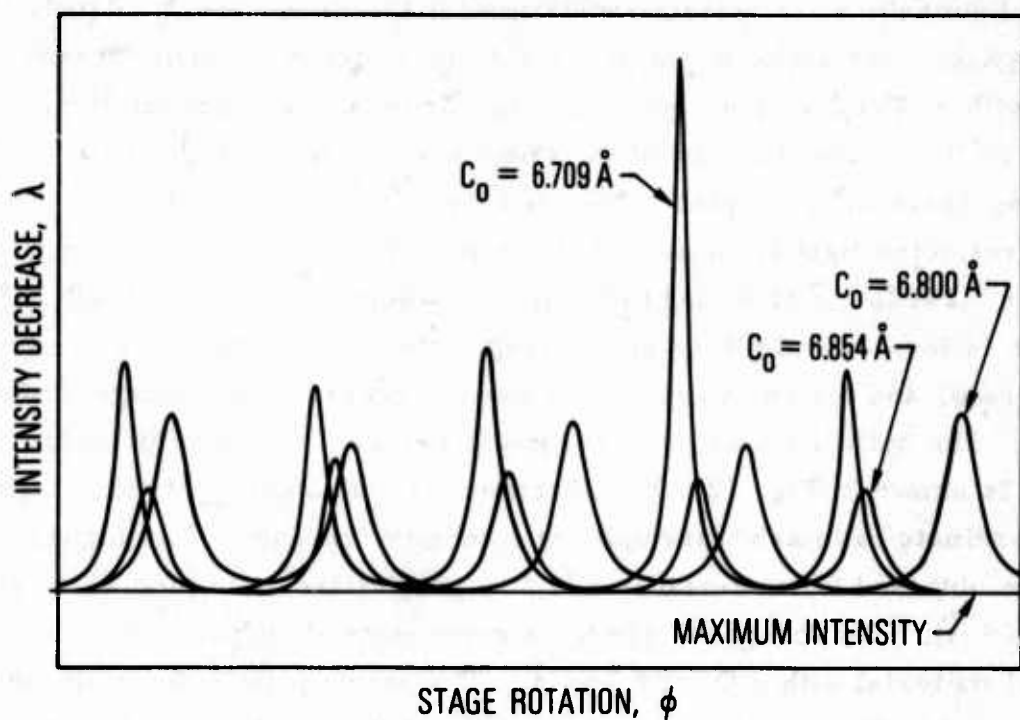
Figure 12. Optical Anisotropy Curves for Various
Pyrolytic Graphites

rocket motor environment. An examination of the thermal expansion excursions for those pyrolytic graphites evaluated as part of this characterization study illustrates this point. Representative data from this task are presented in Fig. 13. The percentage of variation in thermal expansion is considerable, particularly in the shell critical hoop, or ab direction.

C. RESIDUAL STRESS

The single most severe deterrent to the satisfactory use of pyrolytic graphite materials in rocket nozzles as lightweight flame barriers has been the inability to reconcile the residual stress in terms of the deposition process itself, or in combination with the thermally induced rocket motor firing stresses. In other words, if overly high residual stresses do not result in stress cracking during cool down from deposition temperatures, they do result in stress failures during firing. This has been the case to now. In this study, efforts were made to measure residual strains and equate these measurements to the analysis and to the observed microstructure and measured properties. Toward this end, an experimental technique, adapted from the Sachs boring out approach, was developed to monitor dynamically strains as a function of wall thickness for various pyrolytic graphites and combinations of pyrolytic graphite plus substrate materials. The mechanics of this experiment have been detailed elsewhere.[8] Circumferential and axial strains are plotted in Figs. 14 and 15, respectively, for three different structures of pyrolytic graphite deposited in the form of 2-in.-diam, nominal 50-mil-wall, free-standing tubes plus the circumferential and axial residual strains for a 5-in.-diam free-standing tube that contained an anomalous microstructure. These particular results were selected in order to illustrate the disparity of strain levels (and even directions) that can result from changes in the deposition process. This is most graphically demonstrated in Fig. 16, where the inside-diameter tensile strain of a small-diameter nozzle that yields a convoluted configuration on final slicing is compared with the inside-diameter compressive strain of the 5-in.-diam tube. (The compressive strain has caused the tube to spring outward after final stress relief.) Efforts are
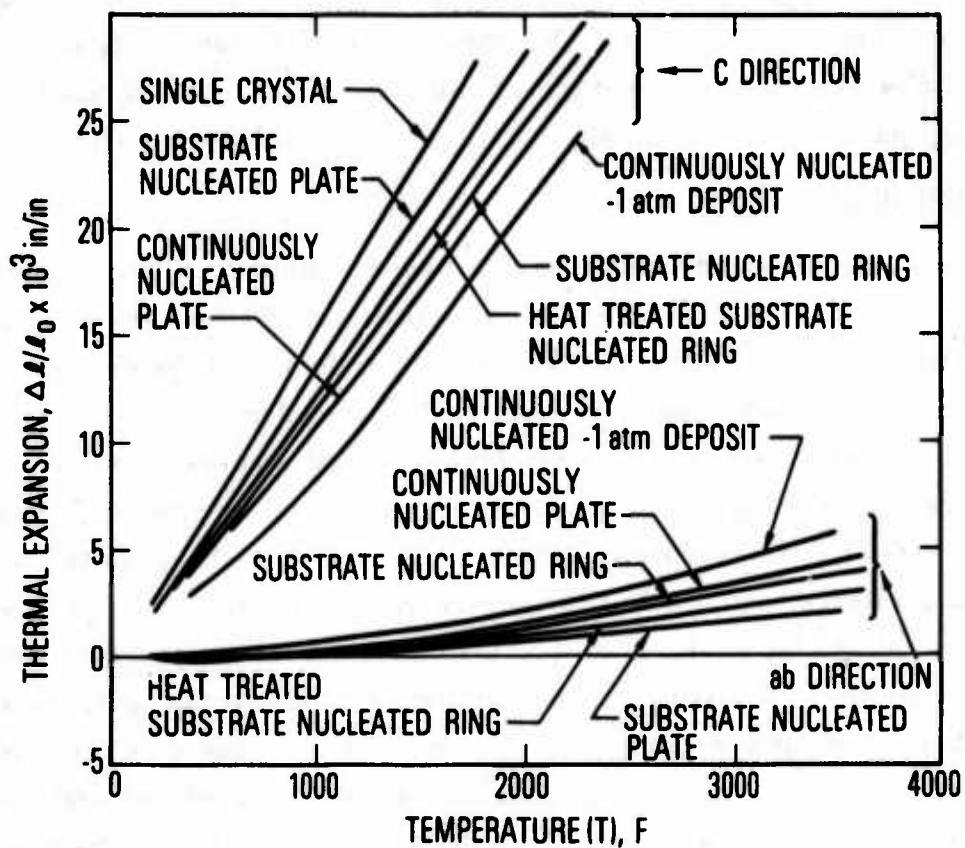
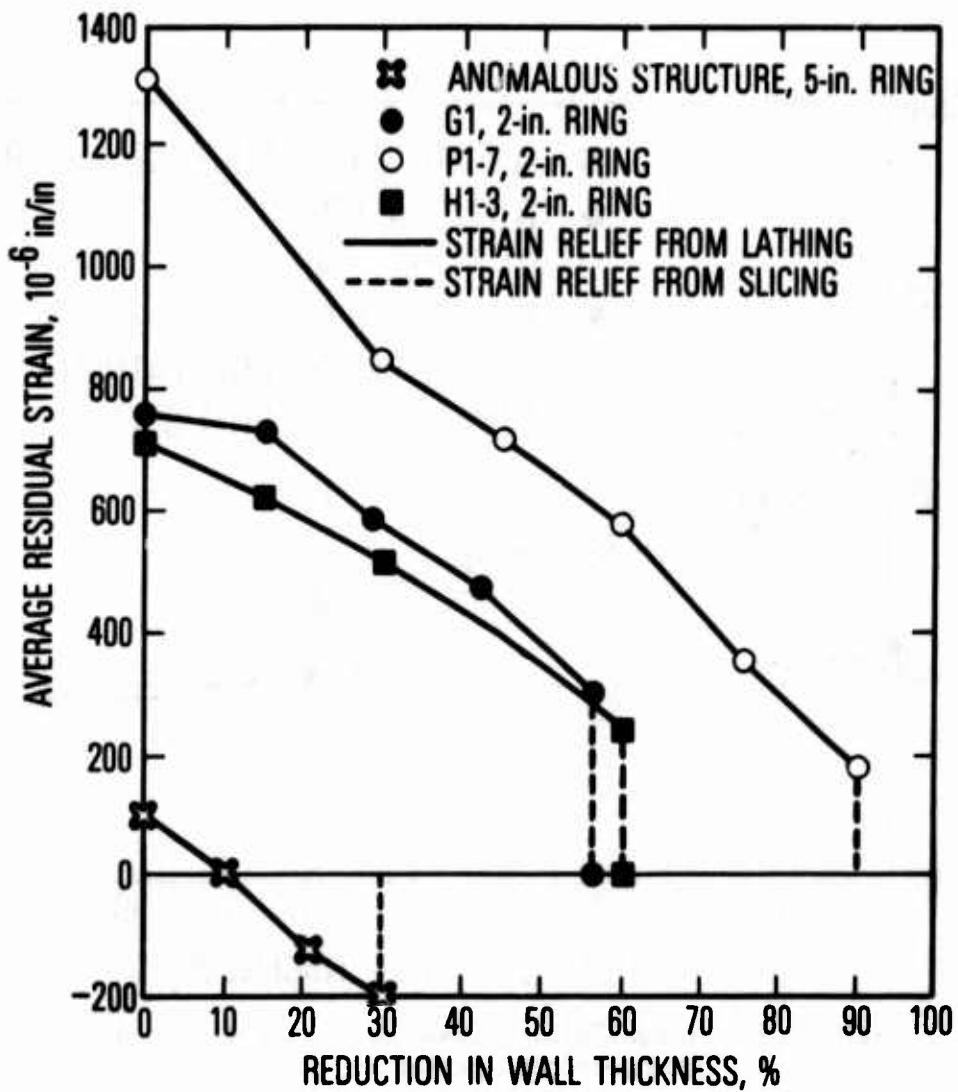Figure 13. Thermal Expansion of Pyrolytic Graphites

Figure 14. Inside Cylinder Surface Circumferential
Residual Strain Relief Profile
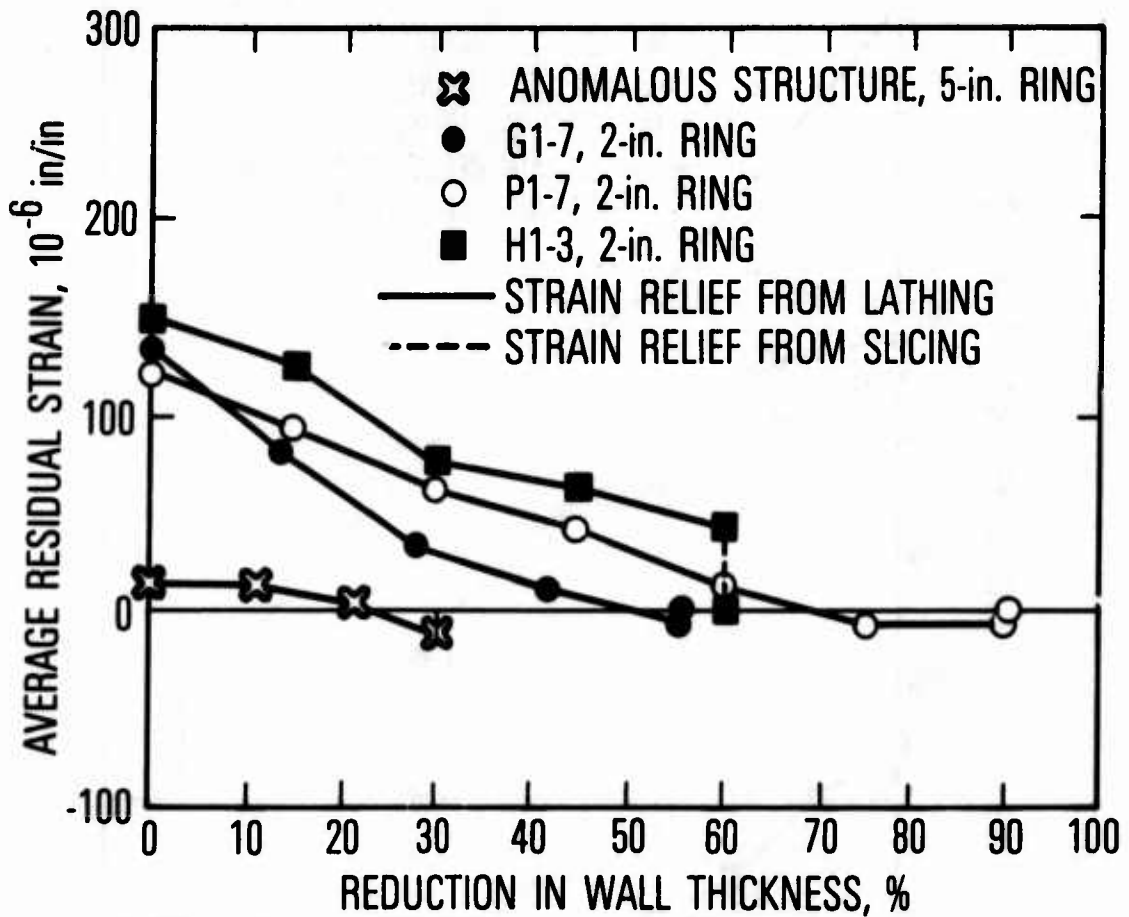
Figure 15. Inside Cylinder Surface Axial Residual
Strain Relief Profile

a   b
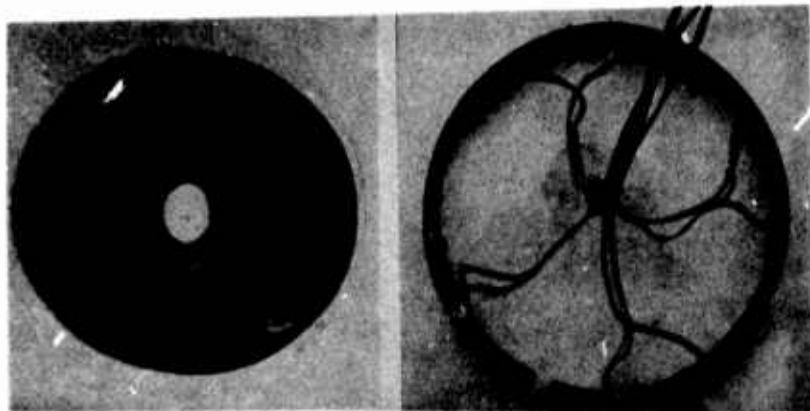
Figure 16. Comparison of Inside-Diameter Tensile
Strain of Small-Diameter Nozzle (a) with
Inside-Diameter Compressive Strain of
5-in. -diam Tube (b)

continuing to define the precise relationship that exists between residual
strains of the as-deposited pyrolytic graphite nozzle shapes and the basic
microstructure. The objective is to allow alternations to microstructures
in order to produce the optimum stress state within the pyrolytic graphite
structure.

IV. CONCLUSIONS

There exists a relationship between the primary structure of both carbon-carbon and pyrolytic graphite materials and the ultimate response of these materials to the rocket motor environment, which can be related to certain key material characteristics. The initial step toward the use of this information to gain an improvement in performance is to define these key parameters. The second step is to measure each characteristic property in sufficient numbers to provide a statistical data base. The third step is to understand the data and their impact sufficient to warrant their use in a program to redefine material requirements. The fourth and final original step is to use the resultant properties or characteristics to tailor or alter material (i.e., carbon-carbon or pyrolytic graphite) structure to achieve the desired ends. Subsequent steps are iterations of the initial five, aimed at optimizing the material characteristics. This program has dealt with step one and initiated step two. The remainder of the process awaits the results of future programs.

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